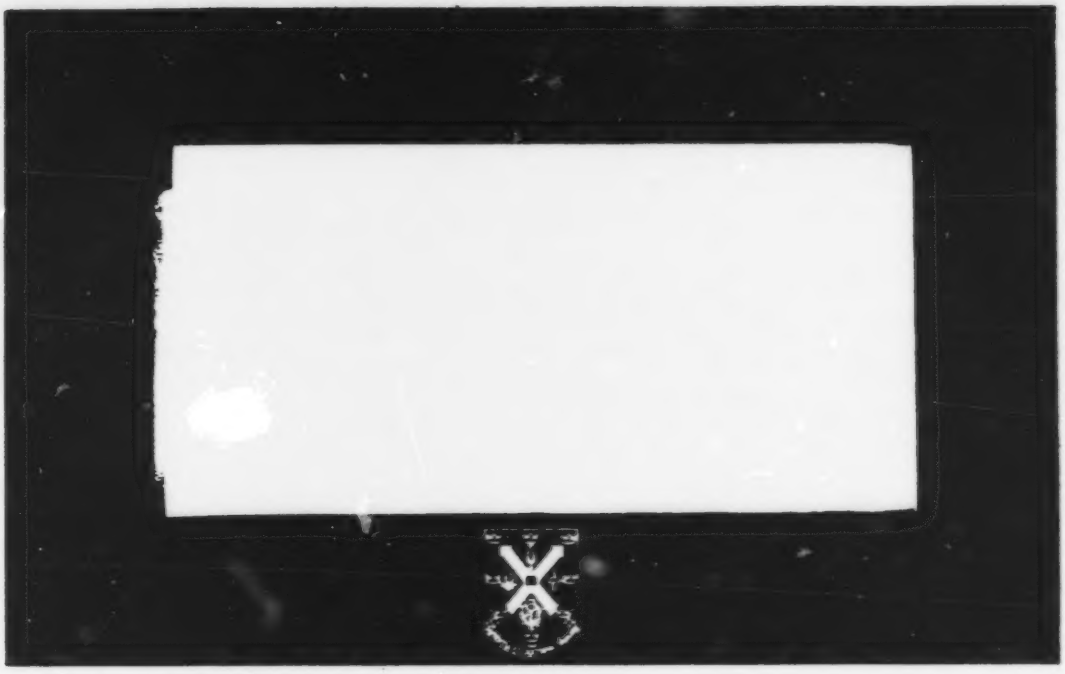

Queen's University at Kingston
Department of Chemical Engineering

PROCESS DEVELOPMENT OF AN INTEGRATED EXTRACTIVE FERMENTATION SYSTEM - PART OF THE BIOENERGY DEVELOPMENT PROGRAM (BDP)

Process Development of an Integrated Extractive Fermentation System - Part of the Bioenergy Development Program (BDP)

RENEWABLE ENERGY DIVISION

PREPARED FOR:
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Coal and Alternative Energy Branch
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OBJECTIVES: To design and operate a larger scale demonstration unit of Queen's Extractive Fermentation Process in order to verify the technical advantages of this process. To develop process improvements. To determine the cost of producing ethanol by extractive fermentation.

RESULTS: Operation of the demonstration unit on a continuous basis for over 400 hours confirmed the numerous technical advantages of extractive fermentation (high reaction rate, reduced water consumption etc. Thermal recovery of ethanol at high concentrations ($\approx$80% wt.) by flash vaporization, and stability of the extracting solvent with negligible losses have been demonstrated. Substrate costs represent the major economic component of ethanol production by extractive fermentation.

CONCLUSION: Extractive fermentation continues to be shown to be a technically superior process and the lead in developing this Canadian technology has been extended.

RECOMMENDATIONS: Improvement of the extractive fermentation process by a straightforward redesign in three system areas would facilitate operation of the process under "optimal" conditions. These optimal conditions could be readily determined by extending the techno/economic simulations to accommodate different scales of operation and varying financial factors. In conjunction with similar simulations of conventional production technologies, a direct demonstration of the economic superiority of the extractive fermentation process could be provided. It is recommended that this work be undertaken.

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PREFACE

This report describes process development, experimental and computer simulation work involving technical and economic aspects of the extractive fermentation process which is being developed at Queen's University at Kingston. The Queen's extractive fermentation unit was the first technically successful process of this type to be reported in the international scientific literature and the present development work was intended to maintain this technological lead. A laboratory-scale research prototype system was scaled up and redesigned to attain a higher degree of sophistication than that previously used, and the economic feasibility of producing fermentation ethanol by this method was examined.

This report will be useful to those interested in the development of technology for the production of fuel ethanol: commercial producers, scientists and economists.

ABSTRACT

A demonstration unit of the prototype extractive fermentation process previously developed at Queen's University was designed and operated to verify the technical advantages of producing ethanol by means of this processing strategy. In additional to further developing and refining the process, operating data were generated which served as part of the basis for determining the cost of producing ethanol by extractive fermentation at a scale of 20×10^6 L/yr of azeotropic (95% by weight) ethanol. High reaction rates, the capability to convert concentrated feeds, the production of a concentrated ($\approx$80% by weight) ethanol stream by flash vaporization, among other advantageous features of extractive fermentation, were demonstrated. Recommendations for process and economic optimization are suggested in order to maintain the Canadian lead in the development of this technology.

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EXECUTIVE SUMMARY

Numerous processing strategies exist for the fermentative production of ethanol. Virtually all of these processes are constrained, however, by the most distinguishing feature of the ethanol fermentation: end-product inhibition. Practically, this is reflected in low fermenter reaction rates (and low productivities), dilute product streams, and large-capacity equipment to deal with the associated high water throughputs. A novel process, extractive fermentation, has been developed in which the inhibitory ethanol product is selectively removed directly from the aqueous fermentation broth by extraction with an immiscible organic solvent. This results in low ethanol concentrations in the aqueous phase, high reaction rates, significantly reduced water consumption, and the prospect of recovering near-azeotropic ethanol from the extracting solvent. The present project was aimed at scaling up and developing a laboratory-scale prototype unit, and determining the cost of producing ethanol by means of an extractive fermentation system.

A Process Development Unit (PDU) was designed, constructed and operated to verify, at a larger scale, the technical advantages of extractive fermentation established with a 1.3 L prototype system. The PDU was based around a continuous flow, 7 L fermentation vessel and, in addition to improved instrumentation, the completeness of the system's design was extended by the addition of a flash vaporization unit for ethanol recovery and solvent regeneration. The process was operated continuously for a period of over 400 hours to demonstrate effective

system performance. An economic analysis of the cost of producing ethanol by extractive fermentation was also performed, based on standard engineering practices and material and energy balance equations formulated, in part, on the results of PDU operation.

The technical benefits of the extractive fermentation of ethanol were verified by the larger scale PDU. Substrate feed concentrations of 30% (by weight) were continuously fermented at up to 96% conversion efficiency. This significantly exceeds the substrate concentration levels that can be converted by conventional batch or chemostat processes. The high reaction rates and reduced water consumption, initially identified in the smaller research prototype, were confirmed.

The recovery of ethanol from the extracting solvent on a continuous basis by means of a single stage flash vaporization unit has been demonstrated for the first time. In addition to developing a simple and effective means of product recovery, it is important to note that the ethanol left the flash vessel at a concentration of 65-90% by weight, with the remainder being occluded water. Such a highly concentrated product has important and favourable economic implications. It is felt that near-azeotropic ethanol could be obtained consistently from a single stage flash vaporization unit with nominal additional process development work.

Perhaps of equal physical and economic importance is the demonstration that the extracting solvent can be recycled through the system with minimal losses and with no detectable deterioration in its physico-chemical properties. The solvent thus retains its efficacy in spite of repeated cycling through the fermentation and thermal recovery vessels, and requires virtually no make-up as a result of chemical deterioration or solubility losses.

Notwithstanding these achievements, certain components of the process could be improved. Superior and more robust system operation would be attained by incorporating a more efficient solvent/aqueous fermentation broth disengagement device in place of the staged settling column, by improving pressure and temperature regulation in the flash unit, and by increasing the overall degree of automated process control throughout the system.

The economic analysis was performed for an extractive fermentation plant with a capacity of 20×10^6 L/yr of azeotropic ethanol and current (mid-1987) prices for materials and utilities. Generally conservative estimates of financial factors were assumed and material and energy balances were developed as much as possible, on the basis of actual operation of the experimental system.

Substrate cost was found to be by far the largest contributor to the cost of producing fermentation ethanol. As a result, a sensitivity analysis was performed in which varying substrate prices were assumed for the determination of the product cost. This approach to the economic analysis is believed to provide a realistic estimate of the ethanol production costs and could be extended to other conditions or modes of operation.

The work conducted under the aegis of the Bioenergy Development Program (BDP) has been a qualified success. The original laboratory-scale extractive fermentation process was successfully scaled up by a factor of approximately five, and the technical attributes of this production strategy were confirmed at the larger scale. A working process demonstration unit has been constructed and two technically important and economically attractive features have, for the first time, been demonstrated:

1. Thermal recovery of a concentrated ethanol product from the extracting solvent stream by a single equilibrium stage;
2. Thermal and chemical stability (with minimal losses) of the solvent during repeated cycling through the system.

Extractive fermentation for the production of ethanol clearly continues to be a superior processing strategy and this work has reinforced Canada's world-wide lead in the development of this technology. As noted above, some component design improvements would certainly yield an increased robustness in the performance of the system and would facilitate operation under truly optimal conditions. These optimal conditions can only be determined by extending the economic simulation work already done to other scales of operation and process designs, and other economic conditions. Extension of these simulations to include an economic analysis of competing technologies would unequivocally demonstrate the economic attractiveness of extractive fermentation. This combination of PDU operation and economic verification will provide compelling inducements for commercializing extractive fermentation technology.

RÉSUMÉ

1. INTRODUCTION

The productivity of conventional ethanol fermentations is limited since high ethanol concentrations in the fermentation broth decrease the ethanol production rate. This is a well known feature of many fermentation processes and is commonly referred to as end-product inhibition. Extractive product recovery is of particular interest in such cases since it may allow for the removal of inhibitory product(s) by solvent extraction. Thus, extractive fermentation has been one of the many technologies proposed in recent years for the continuous production of ethanol (Minier and Goma 1981, 1982; Mattiasson *et al.* 1981; Wang *et al.* 1980, 1981; Gyamerah and Glover 1983; Munson and King 1984). In addition to minimizing end-product inhibition and maintaining high specific growth rates of the ethanol-producing microorganisms, extractive fermentation may facilitate the recovery of ethanol, displacing azeotropic distillation which is traditionally used to separate ethanol from dilute aqueous fermentation broths (Maiorella *et al.* 1981, Keim 1983). Due to the diminished end-product inhibition associated with extractive fermentation, concentrated substrate feeds can also readily be used.

The continuous removal of ethanol from the aqueous phase can be accomplished by solvent extraction either by the *in situ* introduction of the extractant, or by employing an external circulation loop. If extraction is to take place *in situ*, it is imperative that the extracting solvent be completely biocompatible. Unfortunately, very few biocompatible ethanol extractants have been identified. There are two main reasons for this:

1. As a general rule, biocompatible solvents tend to be poor ethanol extractants (Kollerup and Daugulis 1985a);
2. Most solvent screenings have not been very comprehensive or have only concentrated on a few solvent classes (Gill and Ratledge 1972, Roddy 1981, Murphy *et al.* 1982, Playne and Smith 1983, Matsumara and Markl 1984).

Consequently, most reported work on extractive ethanol fermentation has focused on systems where the extractant is not in direct contact with the microorganism. This has been accomplished by employing immobilized cell fermenters followed by ethanol extraction from the cell-free fermentation broth (Minier and Goma 1981, 1982; Gyamerah and Glover 1983), or through the use of a membrane to separate the solvent from the cells (Matsumara and Markl 1984). With such systems, moderately toxic ethanol extractants such as 1-dodecanol and tributylphosphate have been used with some success. One advantage of employing such extractants is that relatively favourable ethanol distribution coefficients can be achieved. A disadvantage is that the fermenter designs are rather complicated.

In work prior to this project, a computer model simulating the extractive fermentation of ethanol was derived (Kollerup and Daugulis 1985b). It provided a convenient means of establishing a sensitivity analysis of the effect on the fermentation process of changing aqueous and solvent dilution rates, ethanol distribution coefficients and substrate feed concentrations. An extensive and comprehensive solvent screening program was then undertaken in order to screen over 1,400 solvents in terms of their predicted physical and chemical properties (Kollerup and Daugulis 1985a). Based on this theoretical screening, 70 solvents were subsequently investigated experimentally. An operational prototype system was developed for extractive ethanol fermentation in a 1.3 L continuous stirred tank fermenter (CSTF) using the

commercially available bulk chemical ADOL® 85 NF , which is manufactured by Sherex Chemical Co. and is comprised largely of oleyl alcohol, as the extracting solvent (Kollerup and Daugulis 1986a; Kollerup and Daugulis 1987). Operation of the prototype system obtained near complete (96%) conversion of a 535 gL^{-1} glucose feed and demonstrated the kinetic advantage of extractive fermentation. The use of a number of other extraction solvents as well as various advantageous process features of the system have been previously detailed (Kollerup and Daugulis 1985c).

This work represented the first successful extractive fermentation process utilizing a CSTF to have been reported in the international scientific literature. In order to maintain a technological lead in the production of ethanol by extractive fermentation, additional process development work at a larger scale, as well as economic analyses, were required.

2. OBJECTIVES

There were two primary objectives in this project:

1. To undertake process development work on a prototype extractive fermentation system previously examined at a 1.3 L scale for the production of ethanol. A larger, 7.0 L system was to be fully integrated (*i.e.* include continuous thermal recovery of the ethanol product), was to possess more sophisticated electronic process controls, and was to be operated to confirm the technical feasibility of extractive fermentation at this scale.

2. To use the data obtained during operation of the above system to generate mass/energy balances, a process flowsheet, and an economic feasibility analysis for the production of ethanol by *in situ* extractive fermentation.

3. METHOD

The project was comprised of two major components: process development and economic analysis.

3.1 PROCESS DEVELOPMENT

Extensive effort was expended in the design, installation and operation of a larger laboratory-scale Process Demonstration Unit (PDU). A process flowsheet for the PDU is shown in Figure 3.1. Tables 3.1 and 3.2 respectively list the legend for and the components of this flowsheet. The fermenter (V_8) is a MBR laboratory chemostat with a working volume of 5.5 L. During system operation, the volume of the aqueous phase in the fermenter was 4.75 L. The extracting solvent, ADOL® 85 NF, is introduced at the bottom of the fermenter through a ring sparger. Due to the difference in densities between the solvent and water, the former rises to form a second phase at the top of the fermenter; the volume of the solvent phase during operation was 0.75 L. The level of the interface between the two phases is set by the position of the inlet to the fermentation broth effluent pump (P_3). The degree of contact between the two phases can be independently controlled by a solvent recirculation loop; a pump (P_5) withdraws solvent from the top phase and returns it to the bottom of the fermenter.

An agitation rate of 150 rpm was found to provide adequate mixing while maintaining a relatively stagnant solvent layer in the upper part of the fermenter, thereby allowing the withdrawal of primarily solvent by the the overflow pump (P_7). The outlet of this pump is the feed

Table 3.1. PDU Flowsheet Legend.

SYMBOLS:

⋈	VALVE
⋈	PRESSURE REDUCING VALVE
⋈	CHECK VALVE
⋈	SOLENOID VALVE
Ⓟ	PRESSURE GAUGE
Ⓥ	VACUUM GAUGE
Ⓣ	THERMOCOUPLE
Ⓕ	FLOWMETER
Ⓡ	RHEOSTAT
Ⓛ	LIQUID LEVEL SENSOR
	ROTAMETER
	FILTER
	AQUEOUS VOLUME
	SOLVENT VOLUME

PHASE WITHIN TUBING:

1	Air. Vacuum. N_2
2	Hot or Cold Water
3	Medium. Aqueous Fermentation Effluent
4	Solvent
5	Ethanol Vapour

Table 3.2. PDU Flowsheet Components.

VESSELS:

V_1	O_2 - FREE NITROGEN CYLINDER
V_2	WATCH GLASS
V_3	SOLVENT REGENERATION COLUMN
V_4	SOLVENT RESERVOIR
V_5	MEDIUM RESERVOIR
$V_6 - V_7$	ACID - BASE RESERVOIRS
V_8	FERMENTER
V_9	STAGED SEPARATION COLUMN
V_{10}	FERMENTER EFFLUENT RESERVOIR
$V_{11} - V_{12}$	FILTER
V_{13}	VACUUM FLASH SEPARATOR
V_{14}	SOLVENT SURGE TANK
V_{15}	CONDENSER COLUMN
V_{16}	CONDENSATE FLASK
V_{17}	REFRIGERATED WATER BATH
V_{18}	VAPOUR TRAP

CONTROLLERS:

C_1	FERMENTER CONTROL
C_2	FERMENTER DRIVE
C_3	VACUUM SEPARATOR FEED TEMP.
C_4	VACUUM SEPARATOR TEMP.
C_5	TIMER

PUMPS:

$P_1 - P_2$	ACID - BASE DOSING
P_3	MEDIUM FEED
P_4	FERMENTATION BROTH EFFLUENT
P_5	SOLVENT RECIRCULATION
P_6	REGENERATED SOLVENT FEED
P_7	SOLVENT EFFLUENT
P_8	EFFLUENT RESERVOIR SOLVENT RETURN
$P_9 - P_{10}$	VACUUM SEPARATOR FEED
P_{11}	REGENERATED SOLVENT RETURN

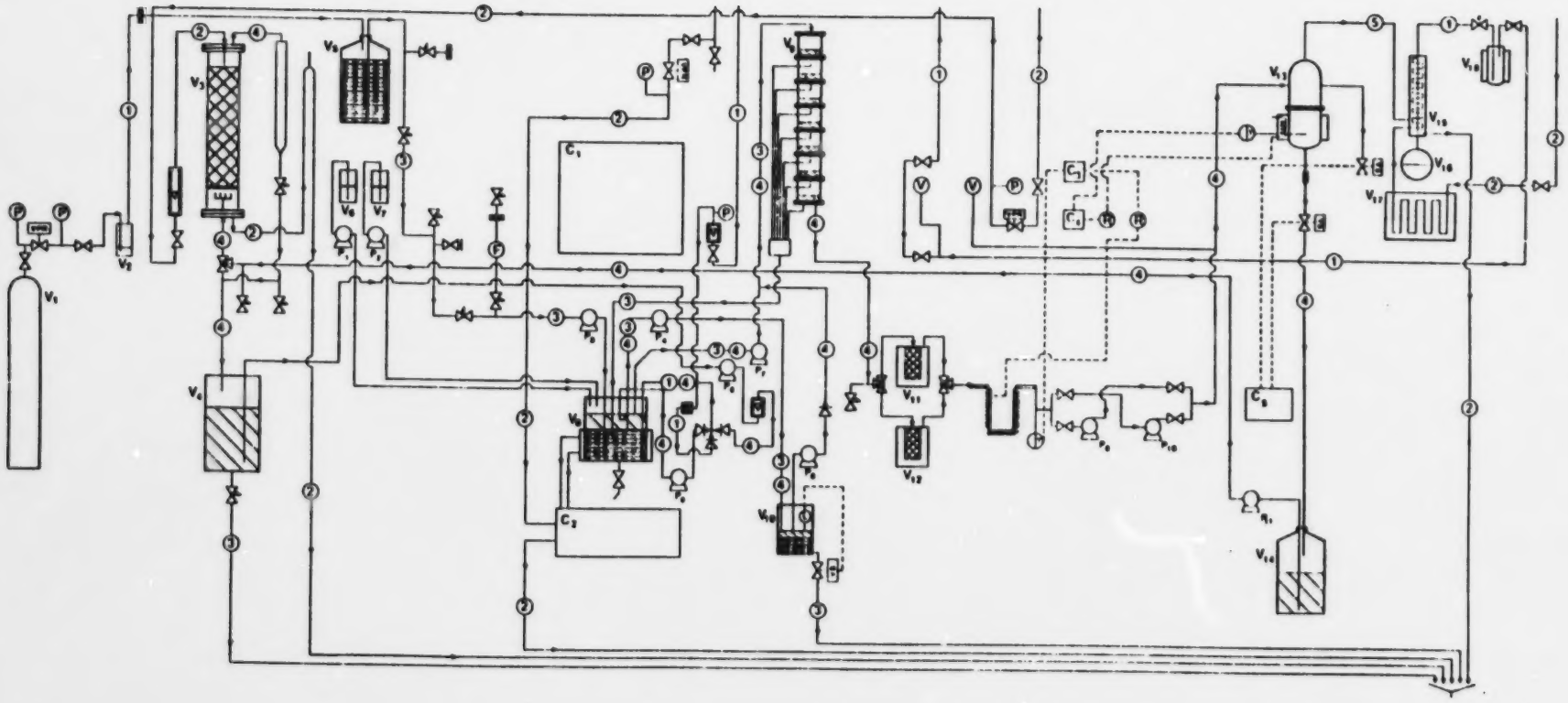

Figure 3.1. Flowsheet for the extractive fermentation Process Demonstration Unit (PDU).

to the staged settling column (V_9) , which returns water and cells present in this stream back to the fermenter. Filters ($V_{11} - V_{12}$) following the staged settler serve to remove any remaining yeast cells before the ethanol-ladened solvent enters the flash vaporization unit (V_{13}). This unit replaced a countercurrent, packed-bed extraction column that had been used to strip ethanol from the solvent using hot water in the 1.3 L system (Kollerup and Daugulis, 198"). The flash unit was operated under a vacuum of 80 kPa at approximately 75°C , conditions at which essentially all the ethanol is removed from the solvent. The ethanol is recovered in the condenser (V_{15}) and the vapour trap (V_{18}) while the regenerated solvent is returned to the solvent reservoir for re-use. The previously used packed-bed solvent regeneration column (V_3) is also incorporated into the present system; however, its use for its original purpose has not been necessary.

Three significant changes in the process layout were made between the time that the flowsheet presented in Figure 3.1 was drafted and the time that testing of the system was completed. They were:

1. A trap was installed in the line between the flash unit (V_{13}) and the condenser (V_{15}) in order to prevent solvent from being entrained into the condenser column and flask.

2. A water/ethylene glycol mixture, flowing in a closed loop through the refrigerated bath (V_{17}), was used as the cooling fluid in the condenser column rather than water from the in-house line. This allowed the bath to operate at a temperature of approximately -10°C .

3. A waste solvent holding vessel and return line were installed to allow the return of solvent from "waste" sources (*e.g.* filter changes). The rate of return was kept low (< 200 mL h^{-1}) in order to avoid upsetting the process. Solvent (and some aqueous waste) reentered the system via the fermenter effluent reservoir (V_{10}).

The PDU was operated with two major objectives in mind: to confirm the technical advantages of extractive fermentation at this scale, and to establish the practicality of thermal recovery of the ethanol product from the solvent stream, as well as the stability of the extracting solvent under repeated use in a closed loop. Thus, the process was operated at a variety of aqueous and solvent dilution rates and with a substrate feed concentration (300 gL^{-1} glucose) exceeding that which could effectively be used by conventional fermentation technologies.

The composition of the medium for the initial batch phase of fermenter operation was: glucose, 150 gL^{-1} ; yeast extract, 10.0 gL^{-1} ; $(NH_4)_2SO_4$, 11.6 gL^{-1} ; KH_2PO_4 , 2.7 gL^{-1} ; $MgSO_4{\cdot}7H_2O$, 0.75 gL^{-1} ; pH adjusted to 4.0. During the continuous operation stages of fermentation, a 300 gL^{-1} glucose feed was used with the salts and yeast extract concentrations being increased proportionally from the above formulation. Medium sterilization of the 150 gL^{-1} medium was accomplished by autoclaving *in situ* for 30 minutes at 121°C . In the preparation of the 300 gL^{-1} glucose feed, autoclaving was not feasible due to the problem of caramelization of the glucose in the medium which is exacerbated at high glucose concentrations and high temperatures. Therefore, instead of autoclaving, oxygen-free nitrogen was flushed through the concentrated media for 30 minutes after its preparation and the head space in the medium reservoir was filled with nitrogen throughout the fermentation in order to minimize the occurrence of surface growth of aerobic contaminants. Submerged contamination by anaerobic microorganisms did not occur in the media, primarily due to glucose inhibition.

The yeast strain employed was *Saccharomyces cerevisiae* NCYC 716 which is a thermotolerant yeast. It was maintained on agar slants and culture transfers were carried out every five months.

During operation of the system, samples were taken from the fermenter's aqueous phase at regular intervals and used to determine cell, glucose and ethanol concentrations, and cell viabilities. During steady-state extractive fermentation, samples of

1. the aqueous phase,
2. the solvent feed to the ethanol recovery unit, and
3. the solvent effluent from the recovery unit

were taken at more frequent intervals and the ethanol concentrations in these streams were measured. The amount of ethanol recovered in the condenser flask and the vapour trap over given periods of time during extractive fermentation was also monitored. Combined with the above ethanol concentrations, this allowed the calculation of ethanol productivities, extraction efficiencies and ethanol losses from the system.

Ethanol concentrations were measured using a Gow Mac Series 750 P gas chromatograph equipped with a flame ionization detector and connected to a Hewlett-Packard 3390 A integrator. The column used was 1.2 m long, 3.2 mm in diameter and was packed with Poropak Q (80/100 mesh). Temperatures of the injector, column and detector were maintained at 160°, 130° and 190°C respectively. Helium was used as the carrier gas at a flow rate of 30 mL min^{-1} . The combustion gases were hydrogen (20 mL min^{-1}) and air (240 mL min^{-1}).

Isobutanol was employed as an internal standard since the ratio of the area of the ethanol peak to the area of the isobutanol peak is linear with ethanol concentrations in the range of 0 to 100 gL^{-1} . Samples taken from the ethanol recovery section of the experimental setup were diluted so that their ethanol concentration fell within this range. Measured ethanol concentrations were accurate to within 5%.

Concentrations of D-glucose were determined using the dinitrosalicylic acid (DNS) reagent method developed by Miller (1959). Experimental samples were measured at 640 nm with a colorimeter after being diluted to achieve a glucose concentration between 0.1 and 1.0 gL^{-1}. Absorbance is close to linear with glucose concentration in this range and measured concentrations were accurate to within 10%.

Cell dry weights were obtained by drying samples at 105°C to constant weight. Cell viabilities were determined by a modified methylene blue staining procedure (Lee *et al.* 1981). This method is based on the fact that non-viable yeast cells will be colored blue in a solution of 0.025% methylene blue in Ringer's Solution (methylene blue, 0.025 g; NaCl, 0.9 g; KCl, 0.042 g; $CaCl_2 6H_2O$, 0.048 g; $NaHCO_3$, 0.02 g; glucose, 1 g; distilled water, to 100 mL) while viable yeast cells will remain colorless when examined using ordinary light microscopy. Yeast cells were counted manually using a standard hemacytometer with yeast culture diluted to an average count of 80-100 cells in the hemacytometer grid.

3.2 ECONOMIC ANALYSIS

The approach to this aspect of the project is based on the work of Maiorella *et al.* (1984) and Kollerup and Daugulis (1986b). The sequence of the work involved:

1. developing a process flow diagram of the extractive fermentation system;
2. specifying operating conditions for the process;
3. formulating and solving material and energy equations for the assumed plant capacity;
4. sizing the items of processing equipment (Peters and Timmerhaus 1980, Perry and Chilton 1973);
5. costing the various items of process equipment at the required capacities using engineering literature (Maiorella *et al.* 1984, Peters and Timmerhaus 1980);
6. assuming financial factors such as return-on-investment and plant life (Peters and Timmerhaus 1980), and determining the current prices of raw materials and utilities;
7. calculating the selling price of the ethanol product.

The above sequence, although tedious and time-consuming, essentially follows standard engineering practice.

Relevant to the above work are the following tables:

- **Table 3.3** lists the operating conditions and process assumptions for the extractive fermentation plant on which the economic analysis was performed and which will be discussed in the next section;
- **Table 3.4** lists the equipment costing equations;
- **Table 3.5** lists financial assumptions used in the economic analysis;
- **Table 3.6** lists the raw material, utility and labour costs used.

It is important to stress that the basis of the economic calculations (the set of material and energy balance equations) was founded as much as possible on our computer model of extractive fermentation whose performance predictions were confirmed by PDU operation, and on the the operating performance of the PDU itself in situations in which model predictions were unavailable (*e.g.* solvent losses, concentration of ethanol product recovered from a single stage flash unit).

Table 3.3. Operating conditions and process assumptions for the extractive fermentation plant process flow diagram (Fig. 4.2).

Parameter		Value
OPERATING CONDITIONS		
Plant capacity	:	20×10^6 L/yr
Ethanol product concentration	:	95 wt %
Operating period	:	330 day/yr, 24 h/day
Nominal feed glucose concentration	:	43 wt %
Residual glucose concentration	:	5.0 g/L
Solvent dilution rate	:	3.0 h^{-1}
Solvent recirculation ratio	:	10 h^{-1}
Solvent residence time	:	1.44 h
Solvent density	:	840 g/L
Ethanol density	:	790 g/L
Ethanol distribution coefficient	:	0.20
KINETIC PARAMETERS		
Maximum specific growth rate	:	0.33 h^{-1}
Substrate saturation constant	:	2.4 g/L
Ethanol inhibition constant	:	29.3 g/L
Cell yield coefficient	:	0.057 g/g glucose
Ethanol yield coefficient	:	0.422 g/g glucose
Carbon dioxide yield coefficient	:	0.501 g/g glucose

Table 3.4. Summary of equipment capacity/cost correlations.

Item	Unit Cost (Canadian dollars)	Capacity unit
Screw conveyors	$MSI \times 0.241 \times CAP^{0.48}$	kg/h
Storage tanks	$MSI \times 0.205 \times CAP^{0.48}$	L
Substrate hopper	$MSI \times 0.121 \times CAP^{0.56}$	L
Fermenter	$MSI \times 0.204 \times CAP^{0.55}$	L
Fermenter agitator	$MSI \times 6.236 \times CAP^{0.67}$	kW
Fermenter cooler	$MSI \times 2.372 \times CAP^{0.32}$	m^2
Air filter	$MSI \times 0.007 \times CAP^{0.67}$	kg gas/h
Air compressor	$MSI \times 8.782 \times CAP^{0.32}$	kg gas/h
Sterilizers	$MSI \times 0.259 \times CAP^{0.55}$	kg water/h
Feed mixing tank	$MSI \times 0.193 \times CAP^{0.56}$	L
Feed agitator	$MSI \times 7.636 \times CAP^{0.65}$	kW
Centrifuges	$MSI \times 0.022 \times CAP^{0.86}$	kg feed/h
Gas absorber	$MSI \times 0.446 \times CAP^{0.60}$	kg gas/h
Rotary dryer	$MSI \times 19.63 \times CAP^{0.47}$	kg evaporated/h
Rotary dryer reboiler	$MSI \times 3.388 \times CAP^{0.48}$	m^2
Stripper/Distillation	$MSI \times 109.9 \times CAP^{0.14}$	kg water/h
Stillage evaporator	$MSI \times 122.5 \times CAP^{0.54}$	m^2
Flash vaporization unit	$MSI \times 20.46 \times CAP^{0.47}$	m^2

Correlations as per Maiorella *et al.* (1984);
MSI = Marshall and Swift Index (mid-198[illegible] = 808).

Table 3.5. Financial and economic assumptions (mid-198" basis).

Plant lifetime	:	25 years
Salvage value	:	$ 0
Return on investment	:	15 %
Annual rate of inflation	:	5 %
Exchange rate	:	$0.76 US/$1.00 CAN

Table 3.6. Material, utility and labour costs (mid-1987 basis).

RAW MATERIALS		
Glucose monohydrate	:	$0.72/kg
Nutrients	:	$0.01/kg glucose
ADOL® 85 NF	:	$3.80/kg
UTILITIES		
Electricity	:	$0.05/kWh
Water	:	$11/1000 m^3
50 psig steam	:	$16/1000 kg
600 psig steam	:	$22.4/1000 kg
LABOUR		
Operating man hours (excluding supervision)	:	$15/man h
CREDITS		
Yeast (50% wt. solids)	:	$0.26/kg
Exhaust steam	:	$2.58/1000 kg

4. RESULTS AND DISCUSSION

4.1 PROCESS DEVELOPMENT

Following extensive testing of the system, an extractive fermentation run of over 400 hours was carried out. Figure 4.1 illustrates the time course of this experiment with respect to the glucose, cell and ethanol concentrations in the fermenter's aqueous phase, **S** , **X** , and $\mathbf{P_A}$ respectively, and the ethanol concentration in the solvent feed to the recovery unit, $\mathbf{P_S}$. Major changes in operating conditions are indicated by vertical dashed lines. Fermentation conditions that were kept constant were: agitation speed 150 rpm; temperature 30°C ; and pH 4.0. Also, during all stages of extractive fermentation, the solvent recirculation rate was 20 L/h.

The different stages of the fermentation were:

I. Conventional Batch Fermentation (0-18 hours).

II. Conventional continuous operation (18-94 hours) with an average aqueous dilution rate of 0.04 h^{-1}.

III. Extractive fermentation (94-186 hours) with an average aqueous dilution rate of 0.04 h^{-1} and an average solvent dilution rate of 1.05 h^{-1}.

IV. Extractive fermentation (186-310 hours) with an average aqueous dilution rate of 0.11 h^{-1} and an average solvent dilution rate of 1.05 h^{-1}.

V. Extractive fermentation (310-432 hours) with an average aqueous dilution rate of 0.15 h^{-1} and an average solvent dilution rate of 2.10 h^{-1}.

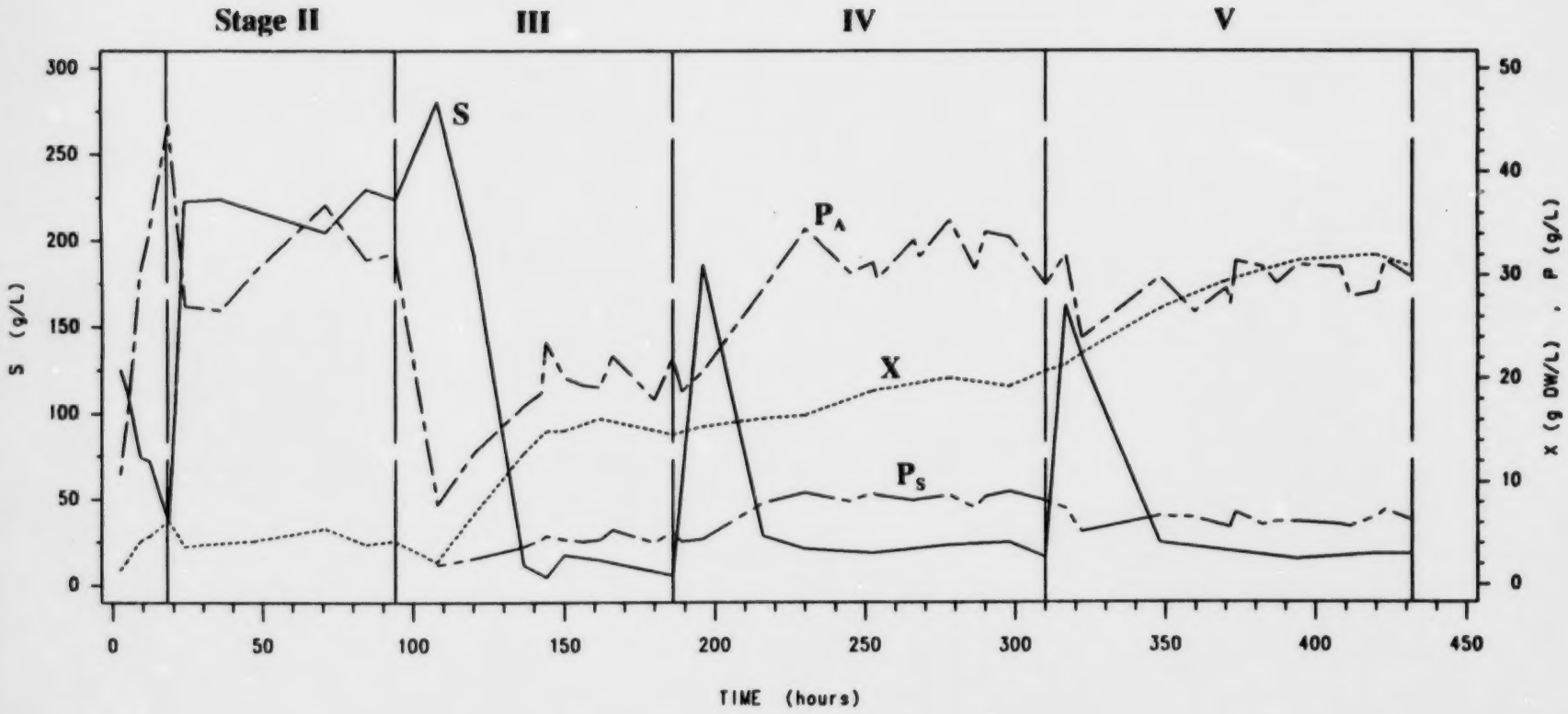

Figure 4.1. Concentrations in the aqueous and solvent phases *vs.* time for extractive fermentation of a 300 g/L glucose feed.

Both the aqueous and solvent dilution rates quoted are based on the aqueous volume of the system; the aqueous dilution rate is also based on the medium feedrate which is greater than the aqueous effluent flowrate due to conversion of the substrate to ethanol.

The steady-state data from the chemostat and extractive fermentation stages are shown in Table 4.1. The **extraction efficiency** is defined as the ratio of the amount of ethanol removed in the solvent stream relative to the total amount of ethanol produced. The values presented represent low estimates of the true extraction efficiency since they were calculated using the influent medium flowrate rather than the lower effluent aqueous flowrate for the fermenter. The **ethanol productivity** of the system is based on the aqueous volume of the fermenter and the amount the ethanol recovered from the solvent stream in the condenser and vapour trap. In **Stage III** of the fermentation, 73% of the ethanol present in the solvent stream was recovered either as condensate or in the trap. During **Stages IV** and V, 89% of the ethanol in this stream was recovered. The major source of ethanol losses was through the vacuum line; the ethanol concentration in the effluent solvent from the recovery unit was found to be consistently in the range of 0.1 gL^{-1}. The composition of the recovered condensate varied between 65-90% (by weight) ethanol, with the remainder being water. The major source of this water was water vapour in air entrained in the line from the staged settler.

Although operation of the PDU was not without incident, the system essentially performed in a manner similar to that of the smaller (1.3 L) scale research prototype. When operating properly, the system was stable, reached steady-state quickly, and confirmed the key performance figures (% substrate conversion, extraction efficiency, productivity *etc.*) previously obtained by the extractive fermentation prototype. This is

Table 4.1. Steady-state data during extractive fermentation of a 300 g/L glucose feed.

	FERMENTATION STAGE			
PARAMETER	**II**	**III**	**IV**	**V**
Fermenter:				
Aqueous Dilution Rate, /h	0.04	0.04	0.11	0.15
Solvent Dilution Rate, /h	--	1.05	1.05	2.10
Residual Glucose Conc., g/L	221.	10.8	22.0	19.0
Aqueous Ethanol Conc., g/L	30.7	19.9	31.9	29.7
Solvent Ethanol Conc., g/L	--	4.6	8.4	6.2
Cell Conc., g/L	4.2	14.7	18.6	30.1
Cell Viability, %	95	84	87	81
Recovery unit:				
Extraction Efficiency, %	--	85	73	75
Ethanol Productivity, g/Lh	--	3.5	7.8	11.6
Mean Ethanol Concentration in Recovered Product, % wt.	--	80	75	78

extremely encouraging given the significant increase in scale of operation and the integration of the process in terms of thermal product recovery and solvent recycle.

During this experiment, the system was being operated with a reservoir of 40 L of solvent, and with the solvent circulating in a closed loop (no bleed, no make-up). There did not appear to be any accumulation of toxic or inhibitory compounds (fermentation by-products) during the more than 14 days that the system was operated in an extraction fermentation mode. Volatile by-products are expected to have been removed from the solvent, along with the ethanol, in the flash unit. It is possible that some non-volatile materials may have accumulated in the solvent over the course of a longer extractive fermentation operation; however, such compounds could have been readily removed by the water stripper (V_3) as long as they were water-soluble (the solvent is virtually insoluble in water: < 30 mg/L at 30°C). No deterioration in the physico-chemical properties of the solvent were observed even though the solvent volume passed through the system (including the flash unit) more than an estimated 50 times.

Although the system worked well, problems did arise because of the inefficiency of the staged settling column (V_9) in removing cells from the solvent feed to the flash. This inefficiency resulted in a heavier than planned load upon the filters and not all of the yeast cells were removed from the solvent stream. This in turn resulted in cellular debris collecting in the solvent reservoir and fouling tubing throughout the system, thereby increasing the need for direct monitoring of the system by operators. A possible solution to this problem at this scale of operation is the replacement of the staged settler by a bench-scale continuous centrifuge. Other process improvements that could be made include a better flash vaporization unit design incorporating a higher level of process con-

trols (to minimize entrainment of the solvent and to provide a more stable temperature and pressure), and more sophisticated process controls throughout the system as a whole.

4.2 ECONOMIC ANALYSIS

A large number of assumptions and arbitrary decisions inevitably form the basis of any economic analysis. Some of the more technical "grey areas" include the relationships between Total Purchased Equipment (TPE), Fixed Capital Investment (FCI) and Total Capital Investment (TCI) costs; plant lifetime and salvage value; administrative expenses; and distribution and marketing expenses. Fortunately, precedents and standard engineering practice can be used as guides to resolve these uncertainties (Peters and Timmerhaus 1980, Perry and Chilton 1973); where possible, these guides and a generally conservative approach to economic analysis were used.

Notwithstanding this, a number of additional decisions which affect the economic analysis were arbitrarily made and these warrant some additional comments.

- **Plant capacity:** A capacity of 20×10^6 L/yr of azeotropic (95% by weight) ethanol was assumed with 330 days/yr and 24 h/day of operating time. This is one-fifth of the size of that assumed in the economic analysis of Maiorella *et al.* (1984). In line with our conservative economic approach, we did not wish to provide extractive fermentation with significant economies of scale which may be unwarranted given this as yet unproven technology.

- **Inflation rate:** An annual rate of 5% was assumed, which directly affects the depreciation cost. The wisdom of selecting this value over a plant lifetime of 25 years is a moot point.

- **Fermentation feedstock and price:** A solid, soluble substrate (glucose monohydrate) was selected because its availability and cost are readily established, particularly in relation to materials such as starch hydrolyzates, cellulose hydrolyzates, *etc*. A sensitivity analysis was performed by assuming three prices for the substrate: \$0/kg, \$0.290/kg , and \$0.703/kg (Canadian dollars). The first price corresponds to a situation in which, through tax incentives or other reasons (subsidized grain, waste carbohydrate), the substrate can be made available at no cost to the producer. The second price corresponds to that used by Maiorella *et al.* (1984) for a large U.S. plant utilizing molasses as its feedstock. The third price reflects the actual cost of glucose monohydrate as of mid-1987.

Figure 4.2 shows the process flow diagram developed and the material balance for an extractive fermentation plant operating at a capacity of 20×10^6 L/yr of azeotropic ethanol. Not shown in Figure 4.2, but included in the material balance and the economic analysis are the aqueous bleed stream from the solvent/broth disengagement centrifuge and some storage facilities. As previously noted, this flow diagram and data reflect the operation of the PDU as much as possible. The mass balance for the plant employs a kinetic model for extractive fermentation with cell recycle developed at Queen's University (Kollerup and Daugulis 1985b, Kollerup 1986) which makes use of kinetic and physical parameters (Table 3.3) established in the 1.3 L prototype system and confirmed in the experimental component of this work.

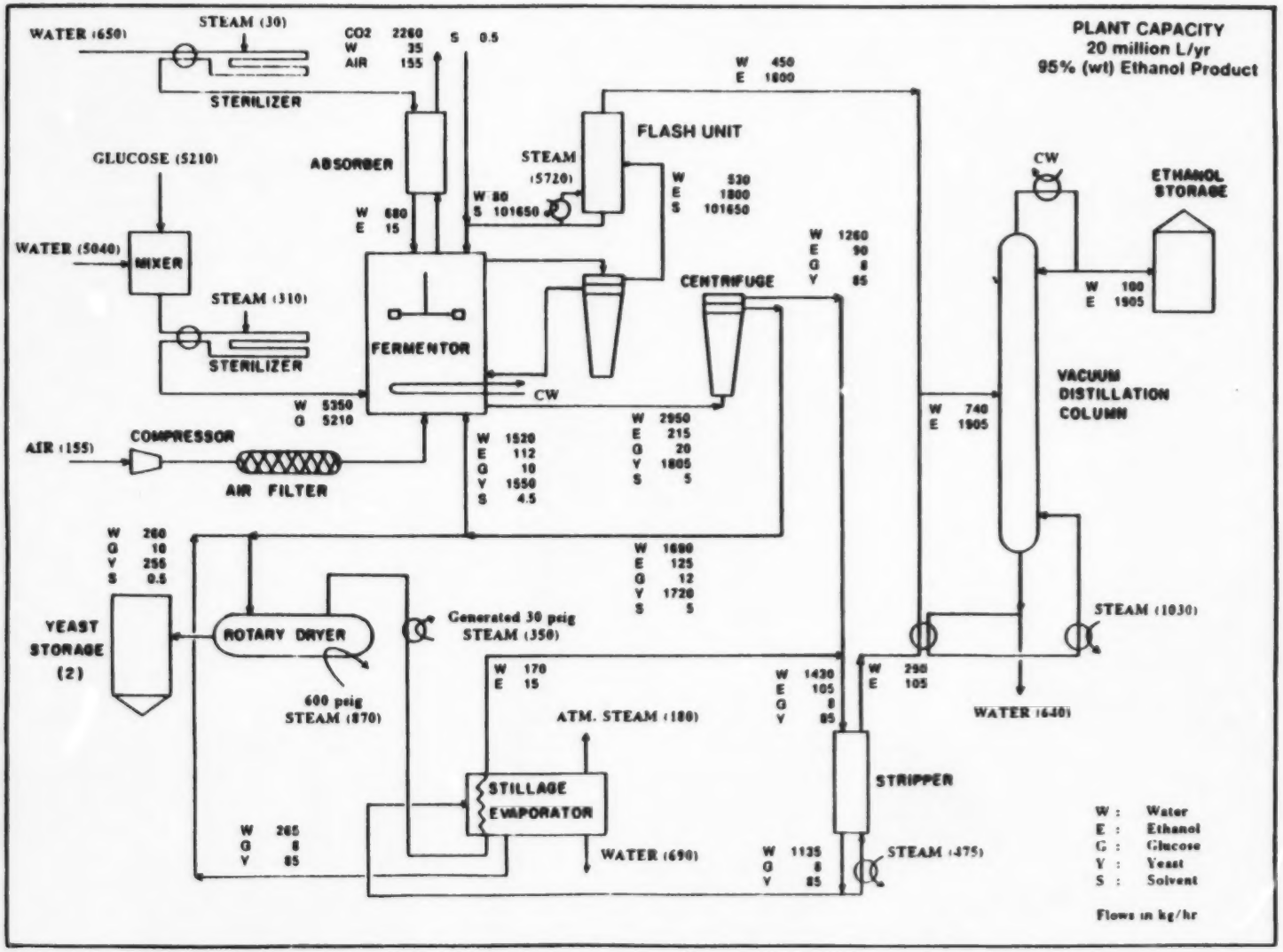

Figure 4.2. Process flow diagram for an extractive fermentation plant with cell recycle.

The fermenter size and product flows are specified according to the fermentation system mass balance; allowances are made for a 15% head space and a 40% increase in the fermenter volume to reflect the additional volume required in an extractive fermenter due to the presence of solvent. A continuous centrifuge, rather than a staged gravity settler, serves to separate out the aqueous fermentation broth and cells associated from the fermenter's effluent solvent stream. This solvent stream is then fed to a single stage flash vaporization unit which recovers a concentrated (80% wt) ethanol product for distillation and the ethanol-depleted solvent is combined with a solvent makeup stream for return to the fermenter.

The effluent aqueous stream from the fermenter is fed to a second centrifuge to allow for cell recycle. To recover ethanol from this centrifuge's supernatant, there is a stripper for initial concentration; stripper vapours and the concentrated ethanol product from the flash unit are combined and fed to a single vacuum distillation column for final product recovery. A portion of the concentrated yeast cream from the cell recycle centrifuge is returned to the fermenter to boost the cell density (and, hence, the reaction rate). The remaining yeast cream is bled from the system and fed to a rotary steam tube dryer to produce a dried animal feed supplement.

Since the cell recycle centrifuge's supernatant is not perfectly clarified, the liquid bottoms from the stripper contain residual cells. This bottom product is concentrated to 25% (wt) solids in a multieffect evaporator and mixed with the yeast cream feed to the rotary dryer. This recycling and recovery eliminates waste streams and removes the need for special waste disposal facilities.

The rotary steam dryer is operated at a high temperature using 600 psig steam to limit the required drying area. The ethanol-water vapours evaporated in the dryer are condensed in the stillage evaporator to decrease the evaporator's steam requirement. In order to recover the residual ethanol from this condensed liquid, it is also fed to the stripper.

The last effect of the stillage evaporator generates atmospheric steam. Additional low-pressure steam is generated from excess heat available from the rotary dryer using a reboiler. It is assumed that low-pressure steam could be used in auxiliary processes and a small credit is take for the steam generated. Credit is also taken for the animal feed supplement produced.

Table 4.2 presents the capital cost breakdown for the process equipment in Figure 4.2, and Tables 4.3, 4.4 and 4.5 show the production cost summaries for the three assumed substrate costs noted above. The most startling result is the fraction of the total cost of producing ethanol by fermentation due to the cost of the substrate. For the case in which the current selling price of glucose monohydrate was used (Table 4.5), substrate costs account for 80% of the total product cost.

The results of this economic analysis beg two questions. Firstly, is the cost of producing ethanol by extractive fermentation the lowest value possible? Secondly, how does the cost of producing ethanol by extractive fermentation compare to that resulting from the use of conventional technology?

Table 4.2. Purchased Equipment Cost Summary

ITEM		COST (mid-1987 basis)
STORAGE		
Glucose hopper	8000 L , CS	$ 14,900
Glucose screw conveyor	0.8 kW, 15 m long	6,100
Ethanol	850,000 L , CS	114,800
Yeast	178,000 L , CS	54,300
Yeast screw conveyor	0.1 kW, 30 m long	3,900
Solvent	40,200 L , CS	26,600
		$ 220,600
FERMENTATION		
Fermenter	64,700 L , SS	75,400
Fermenter agitator	32 kW , SS	51,200
Fermenter cooler	64.3 m^2	7,200
Air filter	155 kg/h air, glass fiber	200
Air compressor	4.1 kW , 30 psig, 155 kg/h air	35,800
Feed water sterilizer	Insulated SS pipes, plus heat exchangers, 5350 kg/h water	23,800
Feed mixing tank	920 L , SS	7,100
Feed mixer agitator	0.9 kW , SS	5,100
Cell-recycle centrifuge	4.7 kW , 5000 kg/h feed	27,200
Initial solvent purchase	$2.89/kg, 40,200 L	128,400
		$ 361,400
ETHANOL RECOVERY		
Absorber	2.5 cm Raschig rings, 2420 kg/h gas	38,600
Absorber-water sterilizer	680 kg/h water	7,600
Rotary dryer	30 m^2 , 1.0 kW , SS , 170 kg/h evaporated	174,600
Rotary dryer reboiler	0.9 m^2 , SS	2,600
Distillation/Stripper	1430 kg/h to stripper, SS combined with conc. product (80 % wt EtOH) and fed to distillation column, CS	245,600
Stillage evaporator	37.2 m^2 , 5 effects , SS	203,800
Single-stage flash	840 m^2, 104,000 kg/h feed, SS	391,600
Centrifuge	141 kW , 111,000 kg/h feed	390,300
		$1,454,700
TOTAL Purchased Equipment - TPE		$2,037,000
FIXED Capital Investment - FCI (4.13 × TPE)		$8,413,000
TOTAL Capital Investment - TCI (4.89 × TPE)		$9,961,000

Table 4.3. Production cost summary ($0/kg glucose monohydrate).

ITEM	NO.	Calculation Method	COST , cents/L (mid-1987 basis)
RAW MATERIALS			
Glucose monohydrate	1	2.00 kg/L EtOH	0.00
Nutrients	2		2.58
Solvent makeup	3	7.7 kg/day	0.05
Raw materials subtotal			2.63
UTILITIES			
Power	4	2.03×10^6 kWh/yr	0.51
Water	5	10.9 kg/L	0.02
Steam	6A	50 psig, 3.36 kg/L	5.38
Steam	6B	600 psig, 0.34 kg/L	0.78
Operating labour	7	$15/man hour, 9 operators	1.79
Supervision	8	15% operating labour	0.27
Maintenance	9	4% fixed capital	1.68
Supplies	10	15% maintenance	0.25
Laboratory	11	15% operating labour	0.27
Direct production cost	A	(= 1 + 2 + ... + 11)	13.58
Depreciation	12	Sinking fund, 25 yr, 0 salvage	0.88
Property taxes	13	3% fixed capital	1.26
Insurance	14	0.7% fixed capital	0.29
Fixed cost	B	(= 12 + 13 + 14)	2.43
Plant overhead cost	C	60% of 7, 8 and 9	2.24
Manufacturing cost	D	(= A + B + C)	18.25
Administrative expenses	15	15% operating labour	0.27
Distribution and marketing	16	5% total production cost	0.97
Total general expenses	E	(= 15 + 16)	1.24
After-tax profit	17	15% return on investment	7.47
Income tax	18	equal to profit	7.47
Yeast credit	19	0.21 kg/L	-5.58
Steam credit	20	0.21 kg/L	-0.05
TOTAL PRODUCT COST	F		28.80

Table 4.4. Production cost summary ($0.290/kg glucose monohydrate).

ITEM	NO.	Calculation Method	COST , cents/L (mid-1987 basis)
RAW MATERIALS			
Glucose monohydrate	1	2.00 kg/L EtOH	58.00
Nutrients	2		2.58
Solvent makeup	3	7.7 kg/day	0.05
Raw materials subtotal			60.63
UTILITIES			
Power	4	2.03×10^6 kWh/yr	0.51
Water	5	10.9 kg/L	0.02
Steam	6A	50 psig, 3.36 kg/L	5.38
Steam	6B	600 psig, 0.34 kg/L	0.78
Operating labour	7	$15/man hour, 9 operators	1.79
Supervision	8	15% operating labour	0.27
Maintenance	9	4% fixed capital	1.68
Supplies	10	15% maintenance	0.25
Laboratory	11	15% operating labour	0.27
Direct production cost	A	(= 1 + 2 + ... + 11)	71.58
Depreciation	12	Sinking fund, 25 yr, 0 salvage	0.88
Property taxes	13	3% fixed capital	1.26
Insurance	14	0.7% fixed capital	0.29
Fixed cost	B	(= 12 + 13 + 14)	2.43
Plant overhead cost	C	60% of 7, 8 and 9	2.24
Manufacturing cost	D	(= A + B + C)	76.25
Administrative expenses	15	15% operating labour	0.27
Distribution and marketing	16	5% total production cost	4.03
Total general expenses	E	(= 15 + 16)	4.30
After-tax profit	17	15% return on investment	7.47
Income tax	18	equal to profit	7.47
Yeast credit	19	0.21 kg/L	-5.58
Steam credit	20	0.21 kg/L	-0.05
TOTAL PRODUCT COST	F		89.86

Table 4.5. Production Cost Summary ($0.703/kg glucose monohydrate).

ITEM	NO.	Calculation Method	COST , cents/L (mid-1987 basis)
RAW MATERIALS			
Glucose monohydrate	1	2.00 kg/L EtOH	140.31
Nutrients	2		2.58
Solvent makeup	3	7.7 kg/day	0.05
Raw materials subtotal			142.94
UTILITIES			
Power	4	2.03×10^6 kWh/yr	0.51
Water	5	10.9 kg/L	0.02
Steam	6A	50 psig, 3.36 kg/L	5.38
Steam	6B	600 psig, 0.34 kg/L	0.78
Operating labour	7	$15/man hour, 9 operators	1.79
Supervision	8	15% operating labour	0.27
Maintenance	9	4% fixed capital	1.68
Supplies	10	15% maintenance	0.25
Laboratory	11	15% operating labour	0.27
Direct production cost	A	(= 1 + 2 + ... + 11)	153.89
Depreciation	12	Sinking fund, 25 yr, 0 salvage	0.88
Property taxes	13	3% fixed capital	1.26
Insurance	14	0.7% fixed capital	0.29
Fixed cost	B	(= 12 + 13 + 14)	2.43
Plant overhead cost	C	60% of 7, 8 and 9	2.24
Manufacturing cost	D	(= A + B + C)	158.56
Administrative expenses	15	15% operating labour	0.27
Distribution and marketing	16	5% total production cost	8.36
Total general expenses	E	(= 15 + 16)	8.63
After-tax profit	17	15% return on investment	7.47
Income tax	18	equal to profit	7.47
Yeast credit	19	0.21 kg/L	-5.58
Steam credit	20	0.21 kg/L	-0.05
TOTAL PRODUCT COST	F		176.50

In answer to the first question, it is extremely unlikely that the analysis represented the optimum conditions for the extractive fermentation process. That is, since there are numerous sets of operating conditions (*e.g.* combinations involving initial and residual substrate levels, aqueous ethanol concentration, solvent and aqueous dilution rates) it is probable that the globally optimal set was not used in this instance. The identification of this set of conditions is both scale and time dependent and would require an optimization study to minimize the objective function of lowest manufacturing cost.

In response to the second question, a similar analysis would have to be performed in order to arrive at an unequivocal answer. As the results of such an analysis would also be scale and time dependent, a meaningful comparison would require identical assumptions applied to the same capacities at a particular instant in time. It should be stressed that once the basic algorithms and form of the process flow diagrams have been established (as has been the case for the extractive fermentation process here), subsequent comparisons and sensitivity analyses can be fairly readily produced.

5. CONCLUSIONS

A considerable amount of effort was devoted to designing, constructing and operating a relatively sophisticated and presentable demonstration unit of the Queen's extractive fermentation process. Operation of the unit was a qualified success. In addition to confirming the technical advantages of extractive fermentation (the capability to utilize concentrated feeds, high reaction rates *etc.*) as originally determined by the 1.3 L prototype system, the process demonstration unit showed for the first time: that a concentrated ethanol product could be thermally separated from the extracting solvent; that the solvent had excellent thermal and chemical stability; and that the system could be operated for a long period of time with minimal losses of solvent. Process improvements could be made, however, in three areas: solvent/broth disengagement; the design of the flash vaporization unit; and the degree of process control throughout the system. We are fully confident that with a few straight-forward alterations in these areas, the process will be able to operate in a robust, effective and trouble-free manner.

Significant effort was also devoted to determining the cost of producing ethanol by extractive fermentation for a plant capacity of 20×10^6 L/yr of azeotropic ethanol. Material and energy balances reflecting PDU operation and current (mid-1987) material and energy costs were employed. As the largest component of the manufacturing cost was the price of the substrate, a sensitivity analysis using varying substrate costs was

performed. A lack of computer power and resources prevented a full optimization study in which manufacturing costs at various sets of operating conditions would have been determined, nor was it possible (due to time constraints) to establish a corresponding production cost using conventional technology. Nevertheless, the approach employed is a rigorous and effective means of establishing the economics of competing technologies and could be readily extended, should greater computer resources become available, to other sets of conditions and scales of operation.

6. RECOMMENDATIONS

Significant advances have been made, both prior to the present project and as a result of the current work, in moving a new fermentation technology from laboratory-scale in a university towards commercialization. Process development work, economic analysis, patent activities and commercial interactions have been components in this overall effort. In our view, however, there remain two additional future activities which, if successfully completed, should provide the final two inducements to commercializing this technology. These two activities are intimately interrelated and would logically form the basis of a research and development program with the following objectives:

1. To determine, by means of computer studies using a process simulator, the optimum (*i.e.* producing the lowest cost) set of operating conditions for the extractive fermentation process at various scales of operation, and to demonstrate the economic superiority of extractive fermentation relative to conventional means of ethanol fermentation at these same scales.
2. To modify the present extractive fermentation demonstration unit as required and to operate the system in order to confirm its ability to perform satisfactorily under the economically optimal conditions as determined by the above.

With these objectives met and with an operational demonstration unit available for inspection, few impediments to commercialization would remain.

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